

NON-CHROMATE METAL SURFACE ETCHING SOLUTIONS

TO WHOM IT MAY CONCERN:

BE IT KNOWN THAT (1) WAYNE C. TUCKER, (2) MARIA G. MEDEIROS, employees of the United States Government, citizens of the United States of America, and resident of (1) Exeter, County of Washington, State of Rhode Island, (2) Bristol, County of Bristol, Rhode Island; and, (3) RICHARD BROWN, citizen of the United Kingdom and resident of Wakefield, Washington County, Rhode Island have invented certain new and useful improvements entitled as set forth above of which the following is a specification:

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3 NON-CHROMATE METAL SURFACE ETCHING SOLUTIONS

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5 STATEMENT OF GOVERNMENT INTEREST

6 The invention described herein may be manufactured and  
7 used by or for the Government of the United States of America for  
8 Governmental purposes without the payment of any royalty thereon  
9 or therefor.

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11 CROSS REFERENCE TO OTHER PATENTS APPLICATIONS.

12 This patent application is co-pending with one related  
13 patent applications entitled NON-CHROMATE COVERSION COATING  
14 (Attorney Docket No. 82602), by the same inventors as this  
15 application.

16

17 BACKGROUND OF THE INVENTION

18 (1) FIELD OF THE INVENTION

19 The present invention relates to a non-chromate metal  
20 surface treating composition for increasing the adhesion of a  
21 metal's surface to any one of a group of layers applied thereto,  
22 such as corrosion resistant layers, and method of applying same.  
23 More particularly, the present invention relates to a metal  
24 surface etching solution wherein a chromate, such as sodium  
25 dichromate dehydrate, or an oxide of chromium, such as chromium

1 trioxide, is replaced with a titanate, namely sodium metatitanate  
2 or an oxide of titanium, namely, titanium dioxide, respectively.

3 (2) DESCRIPTION OF THE PRIOR ART

4 It is known that solutions containing hexavalent chromium  
5 can be used to treat the surface of a metal as etching agents to  
6 increase the adhesion of layers which are subsequently applied  
7 thereto, such as protective coatings. However, although  
8 hexavalent chromium-containing solutions are efficient etching  
9 agents, they are also highly toxic and adversely affect the  
10 environment and human health. For this reason, many chromate-  
11 free solutions for treating metal surfaces have been proposed.

12 Thus, various non-chromate metal surface treatments, such as  
13 disclosed in Tomlinson U.S. Patent No. 5,759,244, the disclosure  
14 of which is incorporated by reference herein, have been disclosed  
15 which can increase the adhesion of a metal's surface to a layer  
16 subsequently applied thereto. Many of these metal treatments are  
17 based on group IV-B metals such as titanium, zirconium and  
18 hafnium. For example, U.S. Patent No. 5,868,872 to Karmaschek et  
19 al discloses a chromium-free aqueous bath solution for non-rinse  
20 treatment of aluminum and its alloys. The solution comprises  
21 zirconium and titanium, orthophosphate, fluoride and a water-  
22 soluble or homogeneously water-dispersible organic film former.  
23 When applied, the solution is dried on the surface of the  
24 aluminum without rinsing. Similarly, U.S. Patent No. 5,897,716  
25 to Reghi et al discloses a chemically and thermally stable

1 chromate-free aqueous liquid treatment for metals which increases  
2 the adhesion of protective layers to the metals' surfaces. The  
3 chromate-free aqueous liquid comprises components selected from  
4 the group consisting of  $H_2TiF_6$ ,  $H_2ZrF_6$ ,  $H_2HfF_6$ ,  $H_2SiF_6$ ,  $H_2GeF_6$ ,  
5  $H_2SnF_6$ ,  $HBF_4$ , and mixtures thereof.

6 The shortcoming of conventional non-chromate metal surface  
7 treatments, such as those described above, is that they cannot be  
8 integrated into and employed in place of chromium-containing  
9 compounds in current metal treatment solutions which otherwise  
10 would contain chromium. As such, conventional non-chromate metal  
11 surface treatments are usually so different from previously  
12 employed chromate-containing metal surface treatments that  
13 significant changes are required to be made in the metal treating  
14 process and in the production of the metal surface treatment  
15 itself. These changes can amount substantial expenditures and  
16 usually require additional approval from Department of the Navy.  
17 Thus, there is a need for "drop-in replacements" that can be  
18 employed in place of chromium-containing compounds, such as  
19 sodium dichromate, now used in conventional chromate-containing  
20 metal treatment solutions. "Drop-in replacement" refers to a  
21 compound that can be employed in a metal surface treatment  
22 solution in lieu of a chromium-containing compound without  
23 requiring any or substantial changes in the make-up of the metal  
24 surface treatment process or metal surface treatment solution.

SUMMARY OF THE INVENTION

1        It is a primary object of the invention to provide a non-  
2        chromate metal surface treatment solution for increasing the  
3        adhesion of a layer, such as a corrosion resistant layer, to a  
4        metal's surface wherein the solution contains a titanate or  
5        titanium dioxide in place of a chromium-containing compound.

6        It is a further primary object of the invention to provide a  
7        "drop-in replacement" for a chromium-containing compound that can  
8        be employed in a metal surface treatment solution which otherwise  
9        would include chromium.

10       Another object of the invention is to provide a method of  
11       increasing the adhesion of a metal's surface to a layer, such as  
12       a protective or corrosion resistant layer, applied thereto.

13       The objects of the invention are accomplished by providing a  
14       highly effective, non-chromate metal surface treatment solution  
15       which includes a titanate, such as sodium metatitanate or  
16       potassium titanate, or titanium dioxide in lieu of a chromium-  
17       containing compound in a metal surface treatment solution that  
18       otherwise would include chromium. More particularly, the  
19       invention relates to a non-chromate metal surface etching  
20       solution for etching metals, specifically, aluminum, aluminum  
21       alloys, stainless steel, titanium and titanium alloys, to  
22       increase the adhesion properties of a particular metal's surface.

23       The present invention is developed on the basis of findings  
24       that the adhesion of a layer or coating, such as corrosion

1 resistant coating, to a metal's surface can be increased by  
2 bathing a metal substrate in an aqueous solution which contains a  
3 chromium-containing compound. Specifically, for example, it is  
4 known that a solution containing distilled or deionized water,  
5 sulfuric acid, seed aluminum and sodium dichromate dihydrate  
6 creates a superb etching solution for aluminum and aluminum  
7 alloys. It is further known that a solution containing chromium  
8 trioxide and deionized water creates a superb etching solution  
9 for stainless steel and titanium. It is believed that the  
10 chromium-containing compound in each of the foregoing etching  
11 solutions provides increased adhesion to the respective metal  
12 surface by providing a contact surface chemistry and allowing for  
13 ionic bonding.

14 Test results show that a metal tested without being treated  
15 with an etching solution has poor durability and weak boundary  
16 layer. For example, untreated aluminum has weak boundary layer  
17 and weak oxides; untreated stainless steel has controlled surface  
18 properties; and untreated titanium has controlled surface  
19 properties. However, since personal exposure limits (PEL) for  
20 chromates is 0.1 mg/m<sup>3</sup> (milligram per cubic meter), chromate-  
21 containing etching solutions are not practical for use. Thus,  
22 "drop-in replacements" for chromium-containing compounds are  
23 needed for etching solutions that otherwise would contain  
24 chromium.

1       Sodium metatitanate, potassium titanate and titanium dioxide  
2   have been found to be well-suited as "drop-in replacements" for  
3   chromium-containing compounds in conventional metal surface  
4   etching solutions which typically include, in addition to sodium  
5   dichromate, potassium dichromate or chromium trioxide, various  
6   other less toxic or non-toxic components. The PEL of the  
7   titanium compounds is 15 mg/m<sup>3</sup>, and thus, the solutions provide  
8   highly effective, non-toxic, metal alternatives to solutions  
9   which otherwise would include chromium-containing compounds.

10

#### 11                   DESCRIPTION OF THE PREFERRED EMBODIMENT

12       The present invention will hereafter be described in detail  
13   with reference to the following embodiments.

14       The preferred embodiments of the present invention are non-  
15   chromate metal surface etching solutions for aluminum, aluminum  
16   alloys, steel and titanium which include a titanate or titanium  
17   dioxide in place of a chromium-containing compound in a metal  
18   surface etching solution that otherwise would include chromium.  
19       For example, it is known that a solution containing 1 liter of  
20   distilled or deionized water, 300 grams of sulfuric acid, 60  
21   grams of sodium dichromate dehydrate and 1.5 grams of seed  
22   aluminum provides an excellent aluminum and aluminum alloy  
23   etching solution. However, as explained above, such chromate  
24   containing solutions pose serious health risks.

1        It has now been found that sodium dichromate dihydrate  
2    present in the foregoing conventional aluminum and aluminum alloy  
3    etching solution can be replaced with sodium metatitanate or  
4    potassium titanate without having to alter the various other non-  
5    chromate constituents therein or the method of employing the  
6    solution. Thus, an etching solution for aluminum and aluminum  
7    alloys that otherwise would contain sodium dichromate dihydrate,  
8    a highly toxic compound, can be rendered non-toxic.

9        In such cases, the aluminum or aluminum alloy to be etched  
10   is first bathed in an etching solution comprising distilled or  
11   deionized water in an amount ranging about 0.5 liter (L) to 1.5  
12   L, sulfuric acid in an amount ranging from about 150 grams (g) to  
13   450 g, sodium metatitanate or potassium titanate in an amount  
14   ranging from about 10 g to about 150 g and bare aluminum in an  
15   amount ranging from about 0 g to about 5 g. The aluminum or  
16   aluminum alloy is immersed in the bath from about 5 minutes to  
17   about 20 minutes while the etching solution is maintained at a  
18   temperature of about 120° F to about 180° F. Immediately after  
19   removing the aluminum or aluminum alloy from the bath, it is  
20   rinsed by spraying it with tap water for about 5 minutes. This  
21   is contrary to prior art methods for applying chromium-free  
22   solution wherein the solution typically is not rinsed from the  
23   metal but rather is allowed to dry thereon forming a polymer  
24   layer. Thereafter, the aluminum or aluminum alloy is soaked in  
25   deionized water and then dried at a temperature of about 120° F

1 to about 140° F. Bonding layers to the metal substrate is  
2 performed within about 16 hours of drying.

3         Similarly, it has been found that titanium dioxide can  
4 replace chromium trioxide in a metal surface etching solution for  
5 stainless steel and titanium which otherwise typically includes 1  
6 part by weight (pbw) chromium trioxide and 4 pbw deionized water.  
7 More particularly, etching stainless steel typically requires two  
8 baths which include two different solutions. For example, a  
9 pretreatment bath or first bath for stainless steel which  
10 includes a solution of 2.5 pbw sodium metasilicate, 1.1 pbw  
11 tetrasodium pyrophosphate, 1.1 pbw sodium hydroxide, 0.3 pbw  
12 nacconol and 95 pbw deionized water is required to clean the  
13 stainless steel. A second bath is further required which  
14 includes an etching solution containing 1 pbw of chromium  
15 trioxide and 4 pbw of deionized water. The present invention  
16 provides a "drop-in replacement" for chromium trioxide in the  
17 foregoing steel and titanium etching solution.

18         Therefore, according to the present invention, stainless  
19 steel to be etched is first immersed in a pretreatment bath  
20 including sodium metasilicate in an amount ranging from about 1  
21 pbw to 5 pbw, tetrasodium pyrophosphate in an amount ranging from  
22 about 1 pbw to 4 pbw, sodium hydroxide in an amount ranging from  
23 about 0.5 pbw to 2.0 pbw, nacconol in an amount ranging from  
24 about 0.1 pbw to 1.0 pbw and deionized water in an amount ranging  
25 from about 90 pbw to 95 pbw. The steel is immersed in the

1 pretreatment solution for about 5 minutes to 15 minutes while the  
2 solution is maintained at a temperature of about 120° F to about  
3 180° F. Thereafter, the steel is rinsed thoroughly in water  
4 before being immersed in a second bath or etching bath which  
5 includes titanium dioxide in an amount ranging from about 0.5 pbw  
6 to about 6 pbw and deionized water in an amount ranging from  
7 about 2 pbw to about 10 pbw. The steel is immersed in the  
8 etching bath from about 10 minutes while the etching solution is  
9 maintained at a temperature of about 140° F to about 190° F. The  
10 stainless steel is then washed in cold running deionized water  
11 and dried in a forced-draft oven at less than 140° F. Thus, like  
12 the etching solution for aluminum and aluminum alloys described  
13 above, the etching solution of the present invention for steel is  
14 not dried thereon thereby forming a polymer layer on the surface  
15 of the steel. Bonding to the stainless steel's surface is best  
16 performed as soon as the metal's surface cools.

17 Etching titanium also requires that the metal be bathed in  
18 two baths that include two different solutions. Typically, a  
19 first bath containing 400 ml (milliliter) of 38% hydrochloric  
20 acid, 40 ml of 85% phosphoric acid and 20 ml of 52% hydrofluoric  
21 acid is required to clean and etch the surface to the titanium.  
22 Thereafter, a second bath is employed which contains an etching  
23 solution comprising 1 pbw chromium trioxide and 4 pbw deionized  
24 water.

1       Therefore, according to the present invention, titanium to  
2   be etched is first immersed in a first bath including a solution  
3   comprising about 350 ml to about 450 ml of a 38% solution of  
4   hydrochloric acid, about 35 ml to about 45 ml of a 85% solution  
5   of phosphoric acid and about 10 ml to about 30 ml of a 52%  
6   solution of hydroflouric acid. Thereafter, it is immersed in a  
7   second bath or an etching bath, like the bath for stainless  
8   steel, which includes titanium dioxide in an amount ranging from  
9   about 0.5 pbw to about 6 pbw and deionized water in an amount  
10   ranging from about 2 pbw to about 10 pbw.

11       More particularly, titanium to be etched employing the  
12   foregoing solutions is first cleaned with a cloth wetted with  
13   trichloroethane in order to degrease the surface. It is  
14   preferred that wiping occurs in one direction only. This serves  
15   to remove dirt. Thereafter, the titanium is immersed in the  
16   first bath or pretreatment bath for about 5 minutes to about 15  
17   minutes at a temperature of about 120° F to about 180° F. The  
18   titanium is then rinsed thoroughly in water before being immersed  
19   in the second bath or etching bath from about 5 minutes to about  
20   20 minutes at a temperature of about 120° F to about 180° F.  
21       Thereafter, the titanium is washed in cold running deionized  
22   water before being dried in a forced-draft oven at 225 ± 25° F  
23   for 1 hour. Again, the etching solution is not dried on the  
24   surface of the metal. The bonding surfaces of the titanium are  
25   primed within about 4 hours of etching.

1        While the preferred embodiment of the non-chromate metal  
2 treatment solution and method of applying same has been described  
3 in detail above, various modifications and variations of the  
4 invention are possible in light of the above teaching. As an  
5 example, the composition of the surface treatment mixtures and  
6 the duration of treatments of various surfaces can be varied  
7 without deviating from the scope of the invention. It is  
8 therefore understood that within the scope of the appended claims  
9 the invention may be practiced otherwise and above described.